

Strong charge transfer effects in the Mg2p⁻¹ core-level spectrum of MgB₂

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Abstract

The two available Mg2p⁻¹ core-level spectra of the recently discovered high-temperature superconducting MgB₂ crystal exhibit interesting structures, but contradict each other. This motivated us to perform *ab initio* calculations on the core-level spectra of cluster models. The computed spectra reveal unusual rich and intense structures triggered by a B2p_z → Mg3s,3p charge transfer.

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INTRODUCTION

The discovery of superconductivity below 39 K in MgB₂ [1] has triggered an avalanche of publications devoted to this and related compounds. The main reason for such an unprecedented interest in MgB₂ is that the mechanism responsible for the transition from a normal to a superconducting state at the remarkably high temperature of 39 K seems to be the conventional BCS phonon pairing [2, 3, 4, 5, 6]. Thus, studying properties of MgB₂ may give a clue to the problem of the high-temperature superconductivity, where numerous scenarios other than phonon pairing have been proposed (see Ref. [7]).

In contrast to the known high-temperature superconductors that contain atoms of *d* and *f* elements, MgB₂ consists of light atoms, which allows one to treat this compound using accurate *ab initio* methods. According to the electronic band-structure calculations reported in the literature [8, 9, 10, 11, 12, 13, 14], MgB₂ can be thought of as a compound made of honeycomb layers of electronically depleted Mg and electronically enriched B (Fig. 1). There are, therefore, spatially separated layers of Mg and B atoms that can play the roles of electron acceptor and donor reservoirs, respectively. Depending on the degree of flexibility of the donor electrons, one may expect a charge instability in MgB₂ with respect to external perturbations. Such kind of instability in MgB₂ may be responsible for the excitation of a collective charge transfer mode theoretically predicted in Ref. [15]. This excitation mode involves coherent charge fluctuations between the B and Mg layers and, according to Ref. [15], may be of relevance for understanding the mechanism of high-temperature superconductivity in MgB₂.

The properties of the ground state of MgB₂ that favour charge transfer processes at low excitation energies may also have an impact on the spectroscopy of highly excited states. In particular, the corresponding valence charge transfer (CT) excitations accompanying ionization of Mg core levels may appear in the spectrum as shake-up (energetically above the intense main line) or even as shake-down (below the main line) satellites. The intensity and the energy of the satellites are controlled by the strength of the coupling between the core hole and the respective valence-excited core-hole configurations and by their relative energies. To zeroth order in the interaction with the core hole, the energy of the satellite relative to the energy of the main state (the state dominated by the single core hole configuration) is equal to the energy of the respective valence excitation in the neutral system. In MgB₂ the

energies of the lowest valence CT excitations are estimated to be 0.5, 2.5 and 5 eV [15]. We, therefore, expect to find low-lying CT satellites in the Mg core ionization spectra of this compound. The available experimentally recorded spectra differ substantially from each other [16, 17]

In the present paper we report an accurate *ab initio* Green's function study of the ionization of Mg2p electrons in MgB₆ and Mg₂B₄ fragments of the bulk MgB₂ (as indicated in Fig. 1). In both clusters the Mg2p spectrum exhibits markedly intense CT satellites at low energies. We also computed the ionization of a related new molecular MgB₆ cluster which is shown to be a stable species at its optimal C_{6v} geometry. The general appearance of the spectral features in this molecular cluster resembles that obtained for the bulk clusters.

DETAILS OF THE CALCULATIONS

Core ionization spectra were computed using the *ab initio* Green's function (GF) method within the algebraic diagrammatic construction scheme (ADC) in fourth order of the Coulomb interaction (ADC(4)) [18, 19]. This method takes into account not only all terms through fourth order but also includes partial summations of diagrams to infinite order. The GF ADC(4) method accurately accounts for orbital relaxation. What is important is that the method maintains a balanced description of orbital relaxation and electron correlation. The GF ADC(4) method has proved to yield a very good description of core ionization [19, 20, 21]. An integral-driven implementation [22] of the original ADC(4) code [23] was used, enabling us to handle cases where the explicit GF matrix would have been too large to compute the whole spectrum (the size of the GF matrices was \sim 2,400,000 for Mg₂B₄ and \sim 1,200,000 for MgB₆ clusters). The Hartree-Fock orbitals and their energies used as input data for the GF ADC(4) method have been calculated using the *GAMESS-UK* package [24] with the 6-311G* atomic basis for B [25] and Mg [26]. In addition, the d function on Mg is selected as prescribed in Ref. [27]. The quality of this medium-sized basis set for the GF ADC(4) core-hole calculations on Mg and Be clusters has been assessed in Refs. [20, 28].

The nuclear geometry in the MgB₆ and Mg₂B₄ fragments of the MgB₂ crystal has been taken from Ref.[1]. The geometry of the MgB₆ molecular cluster has been optimized at the level of fourth-order Møller-Plesset many-body perturbation theory. This results in a planar B₆ ring with a B-B distance of 3.012 a.u. and the Mg atom is situated 3.346 a.u. above the

centre of the ring (C_{6v} symmetry). These distances are slightly different from those of the MgB₆ fragment of the MgB₂ crystal where the B-B distance is 3.367 a.u. and the Mg atom is at 3.329 a.u. above the plane of the B ring. For the crystal structure see Fig. 1.

RESULTS AND DISCUSSION

Our computed Mg2p ionization spectra are shown in Fig. 2 in comparison with the available experimental data. A key finding of our calculations is that the electronic structure of all the clusters responds quite strongly to the creation of the core hole in the Mg2p levels. This strong response is mostly associated with the $B2p_z \rightarrow Mg3s,3p$ charge transfer and manifests itself in the appearance of satellite structures of considerable intensity, which, in the spectra of the MgB₆ clusters, can be seen at energies of $\sim 3, 6$ and 10 eV (Fig. 2). In the spectrum of the Mg₂B₄ cluster the B \rightarrow Mg charge transfer gives rise to a prominent satellite peak at ~ 2 eV, with further structures again at ~ 6 and 10 eV. The satellite peaks have been labelled A, B and C in the theoretical spectra of Fig. 2. It is surprising that, as the figure shows, these intense structures emerge by accumulation of intensity of numerous core-hole states. A general feature of all the spectra is that many low-lying individual shake-up and even shake-down satellites appear, some of them at energies as low as 0.1 eV below the main line, which is defined as the line of highest intensity. The appearance of satellite peak A, especially in the spectrum of Mg₂B₄, is in good agreement with the experimental MgB₂ spectrum of Ref. [16], which also exhibits an intense structure at ~ 2 eV above the main line. This differs remarkably from the other experimental Mg2p spectrum of MgB₂ [17], also shown in Fig. 2. The latter shows an utterly different band shape and only a small hump can be discerned at ~ 2 eV above the maximum of the broad low energy band.

Let us begin our discussion with the Mg₂B₄ fragment cluster. This cluster has the stoichiometry of the bulk MgB₂ and contains atoms of two adjacent unit cells of the crystal (Fig.1). A most intriguing feature of the Mg2p⁻¹ spectrum of the cluster is that there is no isolated main line and actually a dominating main line does not exist at all (Fig.2). At low resolution a dominant peak, which we may denote as main peak, is seen in the spectrum, but this peak is broad and consists of many lines with rather small individual intensities. The most intense among them exhibits an intensity as small as 22% of the total spectral intensity. We encounter here a breakdown of the main line which is very unusual for core

spectra of systems not containing d and f metal atoms. The mechanism responsible for this breakdown, as well as for the appearance of the A, B, and C satellite structures in the spectrum, is a pronounced $\text{B}2\text{p}_z \rightarrow \text{Mg}3\text{s},3\text{p}$ charge transfer.

In the ground state of the cluster an electron has been transferred from the Mg atoms to the borons. The creation of the core hole in the Mg2p level initiates a charge transfer in the opposite direction. By ionizing the Mg2p level the charge is thus transferred back from the boron zigzag to the core-ionized Mg sites. This transferred charge screens the initial core holes giving rise to the appearance of the satellite structures A, B, and C and to the breakdown of the main line. Each of the structures consists of very many individual states which are strong mixtures of singly-excited and doubly-excited core-hole electronic configurations, where in addition to the core hole one or two valence electrons are excited, respectively. In the spectrum, the satellites acquire their intensity by borrowing it from the core-hole configuration. The intensity borrowed is controlled by the strength of the coupling between the core-hole and the excited configurations. Usually, the intensity acquired by states that are dominated by doubly-excited configurations is very small because the coupling of such configurations to the core hole appears only in second order in the Coulomb interaction. By contrast, singly-excited states can acquire considerable intensity in the spectrum because their coupling to the core hole appears already in first order in the Coulomb interaction. In our case the following picture emerges. The valence doubly-excited states appear at energies as low as ~ 2 eV above the main line and their spectral density is much higher than that of singly-excited states. As usual, the intensity is borrowed by the singly-excited states, which are CT states in our case. Due to the presence of the doubly-excited states and their interaction with the singly-excited ones, this intensity is redistributed among the many states available. Therefore, instead of finding a few states with appreciable intensities, we find structures A, B and C, which are considerably broadened by multiple splittings. This mechanism of broadening may also play a role in forming the shape of the spectrum of solid MgB_2 . In the latter case, the peaks may have rather large widths due to the fact that the valence excitations, which in the computed Mg_2B_4 cluster comprise only a limited number of transitions between molecular orbitals, become transitions between electronic bands.

As we mentioned above, a remarkable feature of the spectrum of Mg_2B_4 is that peak A is especially intense and appears at ~ 2 eV above the main line. Its energy and even its intensity relative to the main peak resemble strikingly those of the structure observed at

2 eV in the experimental spectrum of Ref. [16].

The other cluster model of the MgB₂ crystal, the MgB₆ fragment, does not have the stoichiometry of MgB₂ but contains the main structural motif of the B layers of the crystal, that is the B₆ planar ring. The physics of core-ionization of this cluster is similar to that found for Mg₂B₄. Strong B2p_z →Mg3s,3p charge transfer processes are responsible for the appearance of the satellite structures A, B and C in the Mg2p⁻¹ spectrum. These structures consist of many lines with small individual intensities, as in the case of Mg₂B₄. We observe also in MgB₆ a breakdown of the main line; however, this breakdown is not as pronounced as that encountered in the Mg₂B₄ cluster.

The spectrum of the molecular MgB₆ cluster resembles to a large extent the spectrum of the MgB₆ fragment of the MgB₂ crystal (Fig. 2). This is not very surprising because the geometry of the MgB₆ molecular cluster is rather close to that of the MgB₂ crystal. Similarly to the MgB₆ and Mg₂B₄ fragments, the B2p_z →Mg3s,3p charge transfer is responsible for the appearance of intense satellite structures in the spectrum. The structure of the MgB₆ molecular cluster is of particular interest. According to our calculations the B₆ planar ring alone is not stable. This ring is, however, stabilised by the electronic charge transfer from the Mg atom to the boron ring in the ground state of MgB₆. The similarity of the geometry of this cluster to that of the crystal indicates that this mechanism may also be of relevance for the stabilisation of the crystal structure of MgB₂.

A general feature of the Mg2p core hole screening in all our clusters is that the B2p_z →Mg3s,3p charge transfer processes are dominant. Interestingly, the related valence B2p_z →Mg3s,3p charge transfer excitations have been shown to be of importance for understanding the mechanism of high-temperature superconductivity in MgB₂ [15]. Our calculations show that the B2p_{x,y} →Mg3s,3p charge transfer processes make only minor contribution to the screening of the core hole. According to the band structure calculations, σ (B2p_{x,y}) states, which are quasi-two-dimensional σ states, form the metallic properties of MgB₂ [8, 9, 10, 11, 12, 13, 14].

According to our calculations, the total intensity borrowed by satellites is ∼ 60% in the spectra of the MgB₆ clusters and ∼ 80% in the spectrum of Mg₂B₄. This high satellite to main line intensity ratio is not typical for light element compounds where satellites usually acquire ∼ 20-30% of the total spectral intensity. In this respect the clusters studied here can rather be related to the class of strongly correlated systems. These include also known

high-temperature superconductors. Another feature of the Mg-B clusters, which they share with these superconductors, is that the main mechanism responsible for the appearance of intense satellite structures in the core-level spectra is a charge transfer mechanism.

It is worthwhile to discuss the experimental $\text{Mg}2\text{p}^{-1}$ spectra. The band shapes of the two experimental spectra available in the literature are very different from each other (Fig. 2). According to Ref. [16], the surface of the prepared *c*-axis oriented thin film of MgB_2 grown on an *R*-plane sapphire was initially contaminated with different Mg oxides, hydroxides and carbonates. The ionization of the Mg2p level in these compounds contribute to the bulk MgB_2 spectrum at energies of ~ 2 eV. The experimental spectrum (b) shown in Fig. 2, however, has been measured for the MgB_2 surface cleaned by non aqueous chemical etching. The authors of Ref. [16] claimed that the etching yields the high-quality surface free of surface compounds. They demonstrated that the intensity of the 2 eV peak in the spectrum indeed decreases considerably after the etching but this peak does not disappear entirely.

The authors of Ref.[17] also measured the $\text{Mg}2\text{p}^{-1}$ spectrum from a thin film of MgB_2 grown on an sapphire substrate. In contrast to the spectrum (b) [16] there is only a small hump observed in the spectrum (a) at 2 eV above the most intense peak (Fig. 2). That is not the only difference between the (a) and (b) experimental spectra. The spectrum (a) reported in Ref. [17] clearly exhibits an intense line at ~ 1 eV below the most intense peak. There is no similar structure in the spectrum (b) [16]. It should be noted that the MgB_2 film was grown by the authors of Ref. [17] using a method different from that of Ref. [16]. The authors of Ref. [17] claimed that their MgB_2 surface was initially clean, in contrast to the film obtained initially in Ref. [16].

It is not clear why the two experimental spectra have so different band shapes. There can be still impurities in the prepared MgB_2 samples or there may be structural irregularities specific to each of these experiments. We should note, however, that the spectrum (a) seems to be a superposition of the spectrum (b) and some other structure contributing to the spectrum at ~ 1 eV below the highest peak (Fig. 2). The absolute energy of the peak maximum is the same in both experimental spectra. Based on our *ab initio* calculations alone, we cannot identify the factors which make the experimental spectra measured in Refs. [16, 17] so different. Obviously, this situation should be clarified experimentally. Our calculations support the experimental results reported in Ref. [16].

We have calculated the spectra of clusters of limited size. Upon increasing the size of the

cluster, one can expect changes in the spectral bandshapes. According to our analysis one of the effects related to the size of the cluster is the broadening of the satellite structures, and also some additional structures can appear in the spectra of larger clusters. We argue, however, that these changes cannot be significant. The main mechanism responsible for the complicated structure of the spectra of the clusters is the B \rightarrow Mg charge transfer. The strength of this process, and consequently the intensity of the corresponding lines in the spectrum, is controlled by the overlap between the B2p and Mg3s,3p orbitals. Therefore, charge transfer from B atoms which lie near the core-ionized Mg site make the dominant contribution to the screening of the Mg2p core hole, whereas charge transfer from boron atoms far away from the core-ionized Mg atom cannot be strong, due to a small $\langle B2p | Mg3s, 3p \rangle$ overlap. Thus, we do not expect significant modifications of the spectra of larger clusters compared to the spectra of our relatively small ones.

The electronic structure of the MgB₆ molecular cluster sheds some light on the factors stabilising the structure of the MgB₂ crystal. The boron planar honeycomb conformation is stabilised through electron donation from Mg in the ground state of the cluster. In the Mg2p core-ionized states this transferred charge goes back to the Mg site and screens the core hole. The strength of this screening in the molecular cluster is similar to that in the cluster models of the MgB₂ crystal and therefore the core-ionization spectra are similar as well.

To summarize, our accurate *ab initio* Green's function calculations reveal strong many-body charge transfer effects in the Mg2p⁻¹ spectra of the MgB₆ and Mg₂B₄ fragments of the MgB₂ crystal and in the spectrum of the molecular MgB₆ cluster. Three groups of satellites appear in the spectra at \sim 2-3, 6 and 10 eV above the main line. The appearance of the 3 eV peak in our computed spectra and especially of the peak at 2 eV in the spectrum of Mg₂B₄ reflects quite closely the experimental spectrum reported in Ref. [16]. The two experimental Mg2p⁻¹ spectra of MgB₂ available in the literature are very different from each other. This fact, together with the results of our calculations, call for more elaborate experimental studies on the core-level spectra of MgB₂.

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FIG. 1: Crystal structure of MgB₂. The atoms of the Mg₂B₄ and MgB₆ fragments of the MgB₂ crystal studied in the present work are indicated with the indices 1 and 2, respectively.

FIG. 2: The computed Mg2p⁻¹ ionization spectra of the MgB₆, Mg₂B₄ fragments of the MgB₂ crystal and of the molecular cluster MgB₆ in comparison with the experimental data (a) and (b) reported in Refs. [17] and [16], respectively. The relative positions of the experimental spectra have been obtained using their original absolute ionization energy scales. The theoretical spectra were aligned with respect to the position of the peak with the maximal intensity. The vertical lines represent the relative ionization energies and intensities of the computed discrete spectral lines. The band shapes have been obtained by Gaussian broadening of these discrete lines with a half width of 0.8 eV.